Oxidative Dehydrogenation of Ethylenediamine Coordinated to Ruthenium with Hexafluoroacetylacetonate, Induced by Electrochemical Oxidation of Ruthenium(II) to Ruthenium(III)[1)]

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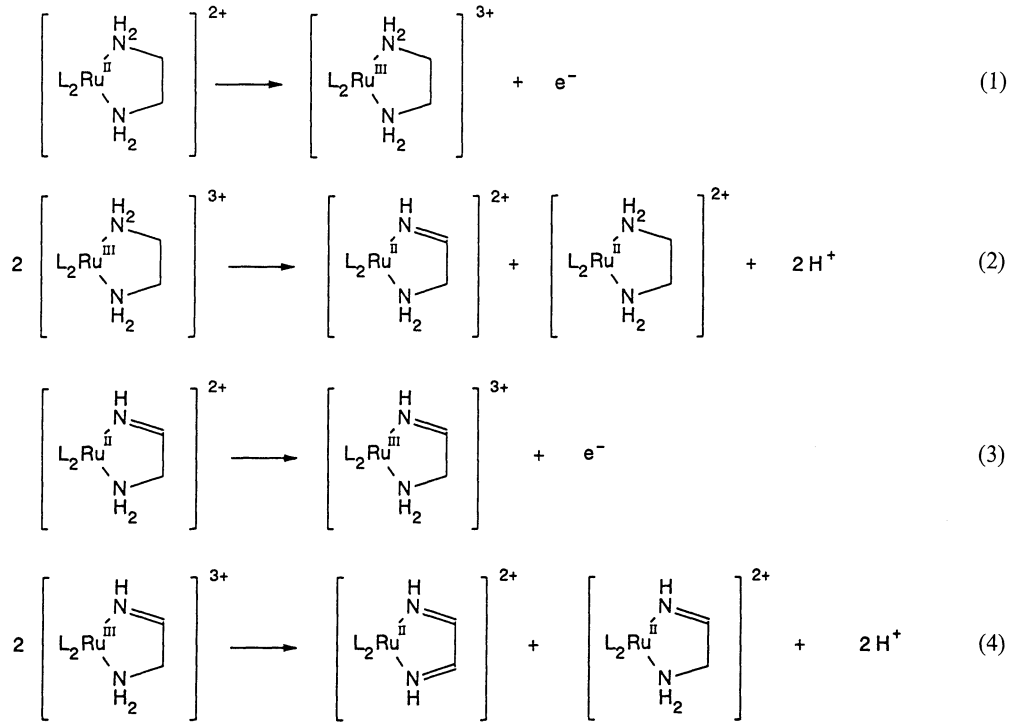
Two mixed-ligand complexes, $[Ru(hfac)_2(en)]$ and $[Ru(hfac)(en)_2]PF_6$ (en=ethylenediamine and $hfac^-$ =hexafluoroacetylacetonate ion), were synthesized. The oxidative dehydrogenation of their en ligand was studied in acetonitrile solutions. Each complex underwent a Nernstian one-electron oxidation at platinum electrodes. The resultant ruthenium(III) species was converted through a series of slow homogeneous reactions into the corresponding 1,2-diiminoethane ruthenium(II) species. Voltammograms recorded during the course of the reactions suggested the presence of 2-amino-1-iminoethane ruthenium(II) intermediates.

Ruthenium(III) ions are known to cause the oxidative dehydrogenation of coordinated amines to imines. The oxidation of ethylenediamine (1,2-ethanediamine, en) coordinated to ruthenium(II) was first reported by Elsbernd and Beattie,[2)] and this peculiar reaction has since attracted the interest of inorganic chemists. Basolo et al.[3)] showed that the reaction involved oxidative dehydrogenation of ethylenediamine to give a 1,2-diiminoethane (dim) ruthenium(II) complex. Several instances of such oxidative dehydrogenations have been reported,[4–10)] but they are limited to the ethylenediamine complexes containing nitrogen-ligating ligands (ammonia,[5,6)] ethylenediamine,[3,4)] 1,10-phenanthroline,[4)] and 2,2′-bipyridine (bpy)[7–9)]). No dehydrogenation of ethylenediamine has been reported for bis(ethylenediamine)dihalogenoruthenium(III),[11–13)] bis(ethylenediamine)oxalatoruthenium(III),[11)] and ethylenediaminebis(oxalato)ruthenate(III)[11,14)] complexes.

The oxidative dehydrogenation of ethylenediamine to diiminoethane is believed to proceed through 2-amino-1-iminoethane (im) ruthenium(II) species (Scheme 1).[7)] This intermediate, however, has not yet been detected.



Scheme 1.

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In this paper, we describe the preparation of two mixed-ligand ethylenediamineruthenium(II) complexes containing hexafluoroacetylacetonate ions (1,1,1,5,5,5-hexafluoro-2,4-pentanedionate ion, $hfac^-$) as an oxygen-ligating ligand: $[Ru(hfac)_2(en)]$ and $[Ru(hfac)(en)_2]PF_6$. Electrolytic oxidation of these complexes in acetonitrile solutions led to oxidative dehydrogenation of the en ligands. Electrochemical observations suggest the formation of the 2-amino-1-iminoethane ruthenium(II) intermediate species.

Experimental

Preparation of the Complexes. (a) $[Ru(hfac)_2(en)]$: Deaerated ethylenediamine (1.06 g, 17.6 mmol) was added to an ice-cooled "ruthenium blue" solution[15] which contained 4.4 mmol of Ru. After the mixture was stirred at 0 °C for 30 min, deaerated Hhfac (1.8 g, 8.7 mmol) was introduced. The mixture was refluxed for 30 min, and then it was concentrated to ca. 20 cm^3 by evaporation; during this procedure, crude crystals separated. These crystals were collected by filtration. All the operations up to this stage were performed under an argon atmosphere, and the filtrate was kept under argon at room temperature. The crude crystals, after being dried under vacuum, were extracted with a mixture of hexane–acetone (5 to 1 by volume). The extract was applied onto a silica gel column (Merck Kieselgel 60, 3.5 cm diameter, 30 cm long) and developed with benzene. The purple-red eluate of the third band was concentrated to ca. 50 cm^3 in a rotary evaporator. The concentrate was filtered, and the filtrate was evaporated on a steam bath. When a precipitate began to appear, a portion of hexane was added. Then lustrous green crystals separated; these were collected by filtration and dried under vacuum: yield 1%. Found: C, 25.15; H, 1.63; N, 4.92%. Calcd for $RuC_{12}H_{10}F_{12}O_4N_2$: C, 25.05; H, 1.75; N, 4.86%. ^1H NMR ($(CD_3)_2CO$) δ=3.05—3.25 (4H, m, CH_2), 4.87 (2H, br., NH_2), 5.02 (2H, br., NH_2), 5.97 (2H, s, CH); ^{13}C NMR δ=47.83 (CH_2), 94.08 (CH), 118.44 (q, $^1J_{CF}$=282 Hz, CF_3), 119.01 (q, $^1J_{CF}$=282 Hz, CF_3), 164.46 (q, $^2J_{CF}$=33 Hz, CO), 167.55 (q, $^2J_{CF}$=33 Hz, CO); UV-vis (CH_3CN; λ_{max}/nm with $\log[\varepsilon/mol^{-1}\,dm^3\,cm^{-1}]$ in the parentheses) 553 (4.26), 516 (sh), 447 (3.80), 289 (4.24), 240 (4.07).

(b) $[Ru(hfac)(en)_2]PF_6$: The filtrate from which crude crystals of $[Ru(hfac)_2(en)]$ had been separated was applied onto a column of SP-Sephadex C25 (3 cm diameter, 4 cm long) and developed with deaerated water. The deep purple-red eluate was again subjected to chromatography with a longer column of SP-Sephadex C25 (3 cm diameter, 18 cm long; developing agent, deaerated aqueous 0.08 mol dm^{-3} NaCl). The purple-red eluate was concentrated rapidly to ca. 5 cm^3 under a reduced pressure. A saturated aqueous solution of NH_4PF_6 was added to the concentrate. When the mixture was cooled, purple-red crystals appeared. The crude crystals were collected by filtration and were recrystallized from acetone–benzene. All the above operations were performed under argon. The crystals were vacuum-dried at 40 °C for 6 d: Yield 4.5%. Found: C, 19.17; H, 2.91; N, 9.56%. Calcd for $RuC_9H_{17}F_{12}N_4O_2P$: C, 18.86; H, 2.99; N, 9.77%. ^1H NMR ($(CD_3)_2CO$) δ=2.60—2.80 (4H, m, CH_2), 3.02—3.22 (4H, m, CH_2), 3.49 (2H, br., NH_2), 4.06 (2H, br., NH_2), 4.93 (2H, br., NH_2), 5.42 (2H, br., NH_2), 5.86 (1H, s, CH); ^{13}C NMR δ=47.18 (CH_2), 46.81 (CH_2), 97.28 (CH), 120.19 (q, $^1J_{CF}$=281 Hz, CF_3), 159.07 (q, $^2J_{CF}$=33 Hz, CO); UV-vis (CH_3CN) 520 (3.90), 288 (3.73), 245 (3.81).

Other Chemicals. Acetonitrile (AN) was purified by distillation.[16] Tetraethylammonium perchlorate (TEAP) was special polarographic grade reagent purchased from Nacalai Chemicals, Ltd., and tetrabutylammonium hexafluorophosphate (TBAH) was prepared according to the literature method.[7]

Measurements. All the potentials were measured against a silver-silver ion reference electrode (Ag|0.1 mol dm^{-3} $AgClO_4$ in AN). All the electrochemical measurements were carried out with a platinum disk electrode (1.99 mm diameter) at (25±0.1) °C as described previously.[16]

Results and Discussion

Voltammetry of $[Ru(hfac)_2(en)]$ and $[Ru(hfac)(en)_2]PF_6$. Each complex exhibited only one anodic step in 0.1 mol dm^{-3} TEAP-AN. The peak separations (ΔE_p) of the corresponding triangular-wave voltammetric peaks were 59 mV for $[Ru(hfac)_2(en)]$ and 67 mV for $[Ru(hfac)(en)_2]PF_6$. Both oxidation steps can be assigned to the Nernstian one-electron oxidation of the central metal ($Ru^{II} \rightarrow Ru^{III}$); the half-wave potentials ($E_{1/2}$) were 0.070 V for $[Ru(hfac)_2(en)]$ and −0.052 V for $[Ru(hfac)(en)_2]PF_6$. No following reaction was detected on the time scale of the triangular-wave voltammetry, but the ruthenium(III) species underwent slow homogeneous reactions, as described below.

Electrolytic Oxidation. (a) $[Ru(hfac)_2(en)]$. A solution of $[Ru(hfac)_2(en)]$ (2 mol m^{-3}) in 0.1 mol dm^{-3} TEAP-AN was electrolytically oxidized at 0.1 V with a platinum gauze electrode. During the electrolysis,

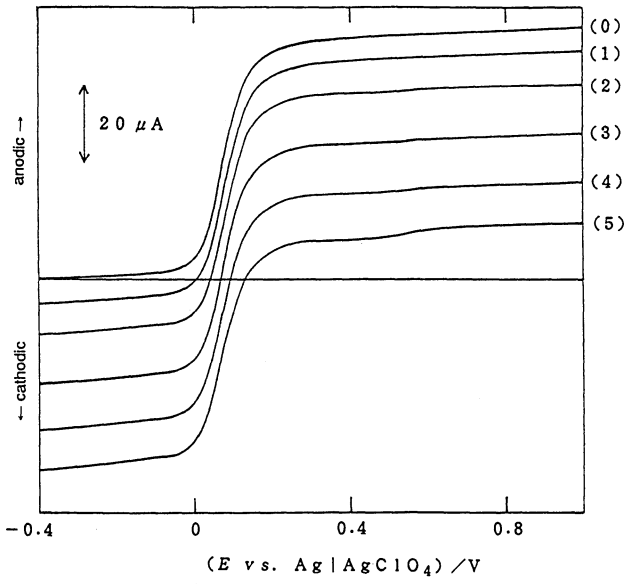


Fig. 1. Change of hydrodynamic voltammograms of 1.59 mol m^{-3} $[Ru(hfac)_2(en)]$ in 0.1 mol dm^{-3} TEAP-AN at 25 °C. Amount of $[Ru(hfac)_2(en)]$, 3.98×10^{-5} mol; rotation frequency, 2500 min^{-1}; platinum disk electrode, 1.99 mm diameter; quantity of electricity/C=0 (0), 0.5 (1), 1.0 (2), 2.0 (3), 3.0 (4), 3.5 (5).

hydrodynamic voltammograms with a rotating platinum disk electrode were recorded intermittently (Fig. 1). In these voltammograms, the anodic diffusion current of $[Ru(hfac)_2(en)]$ decreased, and at the same time, a convective-diffusion controlled, anodic–cathodic mixed step appeared. During the early period of the electrolysis, the height of its cathodic limiting current increased and that of the anodic limiting current decreased linearly with the quantity of electricity, in accordance with a one-electron oxidation. As the electrolysis advanced further, the changes in the current heights began to deviate from linearity. During the time the electrolysis was suspended, the height of the cathodic step, which corresponded to the concentration of $[Ru^{III}(hfac)_2(en)]^+$, decreased slowly. This decrease was accompanied by the growth of two new anodic steps at ca. 0.20 V (not clearly visible in Fig. 1) and 0.55 V; $[Ru^{III}(hfac)_2(en)]^+$ was converted into some oxidizable species.

The solution was allowed to stand for 17 h under an argon atmosphere after being electrolyzed extensively at 0.1 V. At this point, the cathodic step of $[Ru^{III}(hfac)_2(en)]^+$ was still visible; but it was distorted, indicating that some degradation or decomposition had occurred. The two new anodic steps had grown much higher and were now distinct. Then the solution was taken out and evaporated to dryness at 40 °C. The residue was extracted with benzene, and the extract was subjected to column chromatography (Merck Kieselgel 60, benzene). The eluate of the second orange band was collected and was evaporated to dryness. The brown crude crystals were recrystallized from benzene–hexane (5 to 1 by volume).

The isolated product was identified as $[Ru^{II}(hfac)_2(dim)]$ on the basis of the ^1H and ^{13}C NMR data.[17] The triangular-wave voltammograms of this complex in 0.1 mol dm^{-3} TEAP-AN at 25 °C exhibited two pairs of waves: One corresponding to a cathodic process and the other to an anodic process. The cathodic process ($(E_{pa}+E_{pc})/2=-1.52$ V, $\Delta E_p=62$ mV) was a Nernstian, one-electron transfer. It was followed by a relatively slow irreversible reaction, as indicated by the decrease of the corresponding anodic peak current when the sweep rate was decreased to 20 mV s^{-1}. Meyer et al.[7] reported that an electrochemically irreversible reduction of $[Ru(bpy)_2(dim)]^{2+}$ was attributable to the reduction of the diimine linkage. The cathodic process of $[Ru(hfac)_2(dim)]$ is similarly attributable to the reduction of the diimine ligand. The anodic process ($(E_{pa}+E_{pc})/2=0.536$ V, $\Delta E_p=61$ mV) was a Nernstian, one-electron transfer with no following chemical reaction. This process can most likely be assigned to the oxidation of the central metal ($Ru^{II}\rightarrow Ru^{III}$) in view of its Nernstian nature. Its potential was more positive than that of the oxidation of $[Ru(hfac)_2(en)]$ by 0.466 V; this large potential shift appears to reflect an effect of the strong π back donation of the diimine ligand.

Two new oxidation steps appeared when $[Ru(hfac)_2(en)]$ was electrolytically oxidized, as mentioned above. The one at 0.55 V is assignable to the Nernstian one-electron oxidation of $[Ru(hfac)_2(dim)]$ because its half-wave potential is quite close to the mid potential of the triangular-wave voltammetric peaks of the oxidation step of $[Ru(hfac)_2(dim)]$, 0.536 V. Then the other step at 0.20 V will be attributable to the oxidation of $[Ru(hfac)_2(im)]$, which is probably the most stable intermediate of the oxidative dehydrogenation of $[Ru(hfac)_2(en)]$ to $[Ru(hfac)_2(dim)]$. The relative values of the half-wave potentials of these anodic steps (Table 1) seem to support, or at least not to contradict, this view.

If the conversion of one amine to imine in the ligand affected the $E_{1/2}$ value in a simply additive manner, the $E_{1/2}$ of $[Ru(hfac)_2(im)]$ would lie at the midpoint between the $E_{1/2}$ values of $[Ru(hfac)_2(en)]$ and $[Ru(hfac)_2(dim)]$. There is, in fact, another concomitant effect arising from the stabilization caused by conjugation; $[Ru(hfac)_2(dim)]$ has a complete conjugated system, $[Ru(hfac)_2(im)]$ has an incomplete conjugated system, and $[Ru(hfac)_2(en)]$ has none. The ruthenium(II) state, therefore, should be more stabilized in $[Ru(hfac)_2(im)]$ than in $[Ru(hfac)_2(en)]$ and still more in $[Ru(hfac)_2(dim)]$ than in $[Ru(hfac)_2(im)]$. Such stabilization will shift the half-wave potentials of the one-electron oxidation steps of $[Ru(hfac)_2(im)]$ and $[Ru(hfac)_2(dim)]$ to more positive potentials than what would be the case in its absence, but the shift in the case of $[Ru(hfac)_2(dim)]$ should be more than twice the shift in the case of $[Ru(hfac)_2(im)]$.

(b) $[Ru(hfac)(en)_2]PF_6$. The controlled-potential electrolytic oxidation of $[Ru(hfac)(en)_2]PF_6$ was carried out in 0.1 mol dm^{-3} TBAH-AN. The results indicated the presence of a series of chemical reactions following the electron transfer. The following reactions were relatively fast in this case, and the cathodic step of $[Ru^{III}(hfac)(en)_2]^{2+}$ was barely observed on the hydrodynamic voltammograms when $[Ru(hfac)(en)_2]PF_6$ was oxidized at 0 V. When this complex was partially electrolyzed at −0.04 V, two small oxidation steps appeared, at 0.08 V and 0.48 V. For the sake of clarity, the corresponding differential-pulse voltammograms are reproduced in Fig. 2. The peaks corresponding to the above-mentioned new steps are labeled as B and C in Fig. 2b. After exhaustive electrolysis at 0.2 V, both the original peak A and peak B disappeared, but peak C

Table 1. The Half-Wave Potentials of the Oxidation Steps of $[Ru^{II}(hfac)_2(en)]$, $[Ru^{II}(hfac)_2(im)]$, and $[Ru^{II}(hfac)_2(dim)]$ in 0.1 mol dm^{-3} TEAP–Acetonitrile Solution at 25 °C

Complex	$E_{1/2}$ vs. Ag| 0.1 mol dm^{-3} $AgClO_4$–acetonitrile[a]
$[Ru^{II}(hfac)_2(en)]$	0.070[b]
$[Ru^{II}(hfac)_2(im)]$	0.20
$[Ru^{II}(hfac)_2(dim)]$	0.536[b]

a) $E_{1/2}$(ferricinium/ferrocene)=0.025 V. b) Reversible half-wave potential.

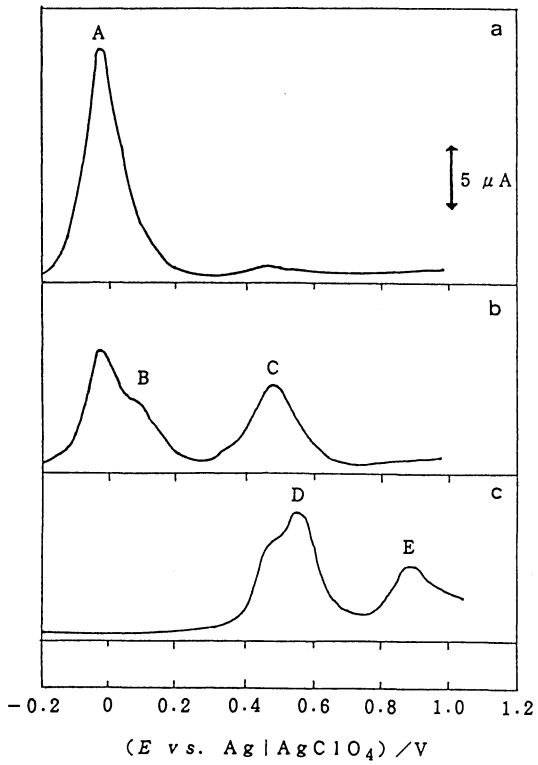


Fig. 2. Differential-pulse voltammograms of 1 mol m^{-3} [Ru(hfac)(en)$_2$]PF$_6$ in 0.1 mol dm^{-3} TBAH-AN at 25 °C. Modulation potential=5 mV; platinum disk electrode, 1.99 mm diameter; a, before electrolysis; b, after partial electrolysis at −0.04 V (platinum gauze electrode); c, after exhaustive electrolysis at 0.20 V, followed by partial electrolysis at 0.45 V.

remained. Further electrolysis at 0.45 V produced two new anodic steps at 0.57 V and 0.88 V (corresponding to peaks D and E in Fig. 2c). When this solution was finally electrolyzed exhaustively at 0.65 V, the differential-pulse voltammogram showed peak E only.

Four new oxidation steps appeared in the case of the electrolytic oxidation of [Ru(hfac)(en)$_2$]$^+$, whereas *two* new oxidation steps appeared in the case of [Ru(hfac)$_2$(en)]. These numbers coincide with the numbers of the amino groups. This fact indicates that the oxidative dehydrogenation reaction also occurred in a stepwise manner in the case of [Ru(hfac)(en)$_2$]$^+$. Peaks B is attributable to the oxidation of [Ru^{II}(hfac)(en)(im)]$^+$, which is produced through the dehydrogenation of [Ru^{III}(hfac)(en)$_2$]$^{2+}$, and peak C to the oxidation of the dehydrogenation product of [Ru^{III}(hfac)(en)(im)]$^{2+}$. This dehydrogenation product will be either [Ru^{II}(hfac)(en)(dim)]$^+$ or [Ru^{II}(hfac)(im)$_2$]$^+$. The relative positions of peaks A, B, and C strongly suggest the former: peak C would be nearer to peak B than to peak D if the bis(im) species underwent the oxidation at peak C, because the shift of the potential brought about by replacement of an en ligand with an im ligand is much smaller (about 0.1 V) than that brought about by replacement of an im ligand with a dim ligand as has been observed in the case of [Ru(hfac)$_2$(en)]. In fact, the difference between peak potentials B and C was 0.4 V, whereas the difference between peak potentials C and D was 0.095 V (Table 2). Peaks D and E appear to be attributable to the oxidations of [Ru(hfac)(dim)(im)]$^+$ and [Ru(hfac)(dim)$_2$]$^+$, respectively. These tentative assignments are summarized in Table 2.

Mechanisms of Oxidative Dehydrogenation of Diamine to Diimine. Meyer et al.[7] proposed a mechanism for the oxidative dehydrogenation of [Ru(bpy)$_2$(en)]$^{2+}$ to the corresponding α,α'-diimine complex as shown in Scheme 1. Here, both [Ru(bpy)$_2$(en)]$^{2+}$ and [Ru(bpy)$_2$(im)]$^{2+}$ are oxidized at the electrode so that the coulometric charge number of the total reaction is four on the basis of the diimine complex, which is in agreement with their experimental value of 3.82.

In our cases, [Ru^{III}(hfac)$_2$(en)]$^+$ and [Ru^{III}(hfac)(en)$_2$]$^{2+}$, the immediate products of the one-electron oxidation, underwent dehydrogenation to the imine and diimine complexes in the absence of electron transfer at the electrode. The nature of the oxidizing agent in this process is not clear from the present experiment. But perchlorate ions are excluded, in view of the fact that the dehydrogenation of [Ru^{III}(hfac)(en)$_2$]$^{2+}$ proceeded in the TBAH medium. It is, therefore, likely that only ruthenium species are involved in the dehydrogenation.

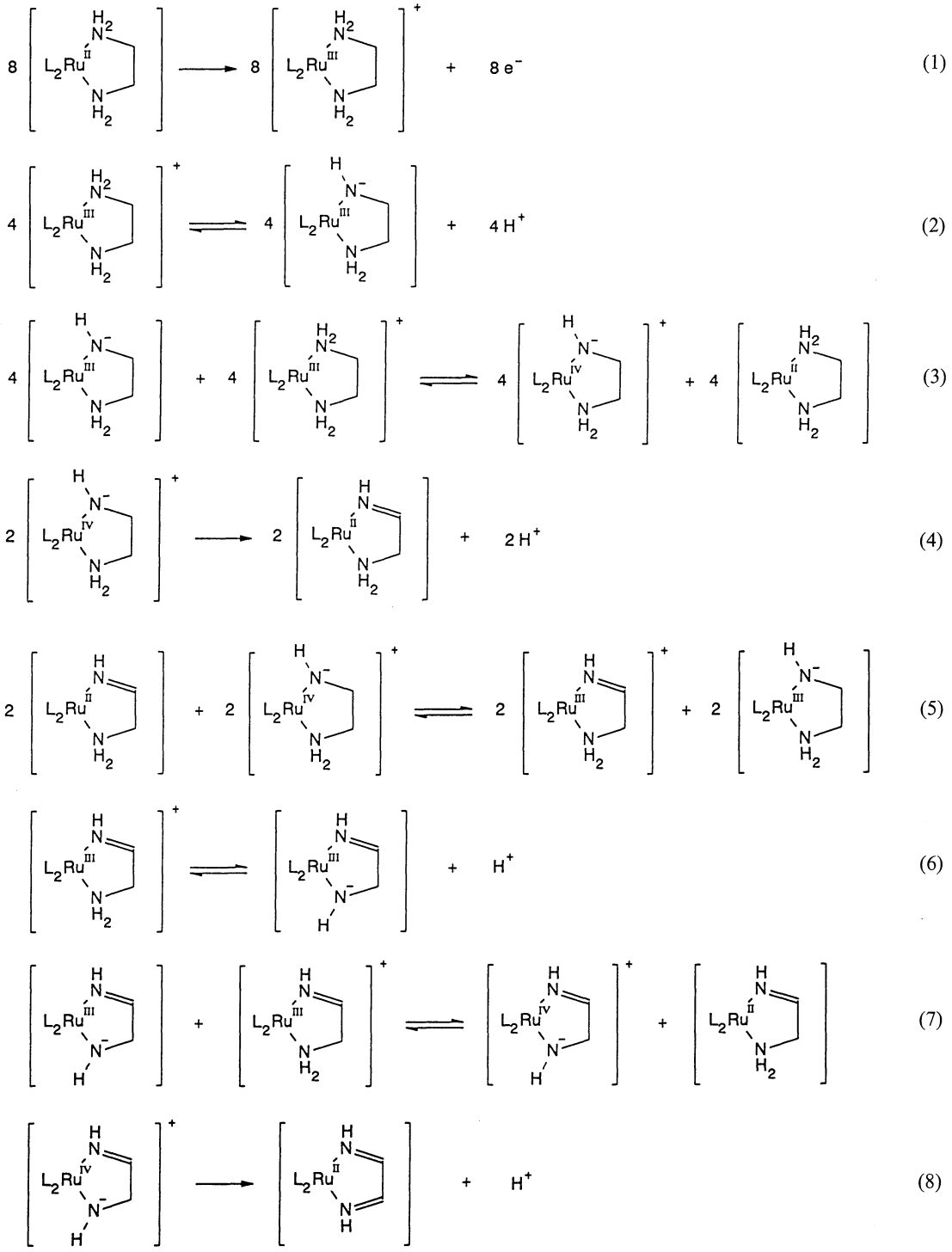
Lay et al.[18] studied the oxidative dehydrogenation of *cis*-1,2-ethanediaminebis(1,2-ethanediaminato(1−)) osmium(IV). They have suggested that their results implicate the metal(IV) oxidation state as an intermediate in the oxidative dehydrogenations of ligands coordinated to Fe and Ru. The oxidative dehydrogenation of [Ru^{II}(bpy)$_2$(ampy)]$^{2+}$ (ampy=2-(aminomethyl)pyridine) by cerium(IV) has been investigated in detail by Keene

Table 2. Assignment of the Oxidation Steps Observed When [Ru(hfac)(en)$_2$]PF$_6$ was Electrolyzed in 0.1 mol dm^{-3} TBAH–Acetonitrile Solution at 25 °C

Peaks	Potentials/V[a]	Electrode reaction
A	−0.021	[Ru^{II}(hfac)(en)$_2$]$^+$⇄[Ru^{III}(hfac)(en)$_2$]$^{2+}$+e$^-$
B	0.078	[Ru^{II}(hfac)(en)(im)]$^+$⇄[Ru^{III}(hfac)(en)(im)]$^{2+}$+e$^-$
C	0.478	[Ru^{II}(hfac)(en)(dim)]$^+$⇄[Ru^{III}(hfac)(en)(dim)]$^{2+}$+e$^-$
D	0.573	[Ru^{II}(hfac)(dim)(im)]$^+$⇄[Ru^{III}(hfac)(dim)(im)]$^{2+}$+e$^-$
E	0.878	[Ru^{II}(hfac)(dim)$_2$]$^+$⇄[Ru^{III}(hfac)(dim)$_2$]$^{2+}$+e$^-$

a) Peak potential on the differential pulse voltammogram against Ag| 0.1 mol dm^{-3} AgClO$_4$–acetonitrile; modulation potential, 5 mV.

et al.[9] They explained the kinetic data in terms of a mechanism involving a ruthenium(IV) species with a deprotonated ampy ligand. An analogous mechanism for the formation of $[Ru(hfac)_2(dim)]$ is presented in Scheme 2. Here, the steps up to $[Ru(hfac)_2(im)]$ are directly based on these authors' mechanism, but the subsequent pathways are only speculative. The proton acceptor(s) appear to be acetonitrile and/or water as a contaminant in the media. This scheme leaves $[Ru^{III}(hfac)_2(HN^{-}-C_2H_4-NH_2)]$ as one of the final products. In facts, this species will decompose eventually; a small quantity of an unidentified bluish by-product



Scheme 2.

was detected in the course of the isolation of [Ru(hfac)$_2$(dim)]. The reaction of [Ru(hfac)(en)$_2$] may be explained similarly. But more experimental investigation is required to clarify the mechanism.

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17) ^{1}H NMR ((CD$_3$)$_2$CO) δ=6.17 (s, 2H, COCHCO), 8.80—8.90 (m, 2H, NH=C<u>H</u>), 13.76 (br., 2H, NH); ^{13}C NMR δ=91.71 (CO<u>C</u>HCO), 117.19 (q, $^1J_{CF}$=283 Hz, CF$_3$), 118.26 (q, $^1J_{CF}$=284 Hz, CF$_3$), 170.24 (NH=CH), 172.38 (q, $^2J_{CF}$=34 Hz, CO), 173.96 (q, $^2J_{CF}$=34 Hz, CO).
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